

Effects of Surfactants on Acrylonitrile Polymerization Initiated by a Cr(VI)–Cyclohexanone Redox System: A Kinetic Study

Manabendra Patra,¹ Ajay K. Behera,¹ Rajani K. Behera,¹ Bijoy K. Sinha²

¹Department of Chemistry, Sambalpur University, Jyoti Vihar, Burla 768019, Orissa, India

²Department of Environmental Science, Sambalpur University, Jyoti Vihar, Burla 768019, Orissa, India

Received 16 August 2002; accepted 1 June 2003

ABSTRACT: The polymerization of acrylonitrile (AN) was kinetically studied with a Cr(VI)–cyclohexanone (CH) redox system as an initiator from 25 to 45° C in the presence of a surfactant. The rate of polymerization and the percentage of the monomer conversion increased as the concentration of the anionic surfactant [sodium dodecyl sulfate (SDS)] increased above its critical micelle concentration. However, the cationic surfactant (cetyltrimethylammonium bromide) reduced the rate considerably at higher concentrations, whereas the nonionic surfactant (TX-100) had no effect on the rate. The effects of the Cr(VI), CH, AN, and H⁺ concen-

trations and the ionic strength on the rates were also examined. The presence of 0.015M SDS reduced the overall activation energy of the polymerization by 5.55 kcal/mol with respect to that in the absence of the surfactant. With increasing SDS concentration, the viscosity-average molecular weight also increased. A suitable mechanistic scheme was proposed for the polymerization process. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1147–1153, 2004

Key words: surfactants; redox system; micellar polymerization; acrylonitrile

INTRODUCTION

The important role of surfactants in polymerization has been studied since the early 1940s.^{1–4} A good amount of work has been done on the polymerization of vinyl monomers in the presence of surfactants with various initiators. Friend and Alexander⁵ observed that different cationic surfactants reduced the rate of acrylamide polymerization initiated by potassium persulfate. They explained it by the assumption that the primary radicals (S₂O₈^{•−}) were bound strongly to a positively charged Stern region of the cationic micelles in comparison with the counterion. The permanganate-initiated acrylamide polymerization rate was also reduced in the presence of a cationic surfactant because of the ion-pair binding of MnO₄[−] with a large cation (RN⁺), which lowered the rate of formation of primary radicals.⁶ Behari and coworkers⁷ observed that the anionic surfactant [sodium dodecyl sulfate (SDS)] enhanced the rates, whereas the cationic surfactant [cetyltrimethylammonium bromide (CTAB)] reduced the rates considerably for persulfate-initiated acrylamide polymerization in agreement with the results of Hussain and Gupta.⁸ A scant amount of work

has been reported on acrylonitrile (AN) polymerization in the presence of surfactants with a metal-ion organic substrate redox system as an initiator. Earlier, we reported the effects of surfactants on the kinetics of AN polymerization with Ce(IV) and V(V) as an initiator in the presence of cyclohexanone (CH).⁹ This article mainly deals with the kinetics of AN polymerization initiated by a Cr(VI)–CH redox system in the presence of SDS and CTAB above their critical micelle concentrations (CMCs).

EXPERIMENTAL

Materials

AN (Merck) and CH (Fluka) were distilled under reduced pressure. SDS and CTAB (Sisco Chem.) were purified by standard methods. Chromium trioxide, TX-100, sulfuric acid, and sodium bisulfate were quality chemicals and were used as such without further purification.

Methods

The experimental setup and kinetic procedure were similar to that of our earlier reports and other work published elsewhere.^{9–12}

Molecular weight determination

The viscosity-average molecular weight (*M_v*) was determined viscometrically. A solution of the polymer

Correspondence to: M. Patra (patramana@hotmail.com).

Contract grant sponsor: UGC (New Delhi, India).

Contract grant sponsor: DST (New Delhi, India).

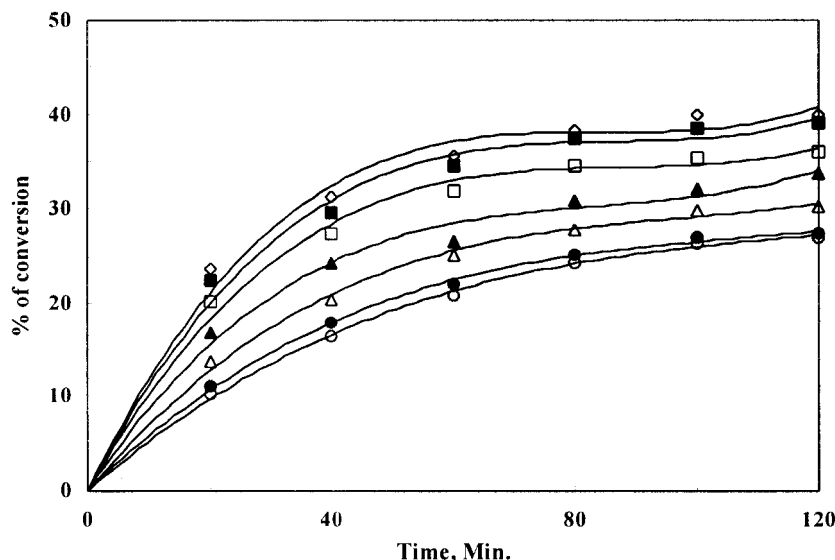


Figure 1 Dependence of the monomer percentage on time. [AN] = 0.518M; [Cr(VI)] = 5.01×10^3 M; [CH] = 0.108M; [H⁺] = 0.498M; μ = 0.6M; temperature = 35°C (○) [SDS] = 0.000M, (●) 0.005M, (△) 0.010M, (▲) 0.015M, (□) 0.020M, (■) 0.025M, or (◇) 0.030M.

(1%) in dimethylformamide was placed in an Ubbelohde suspended-level viscometer. The flow times of the solutions and the solvent were measured at 25°C. The intrinsic viscosity ($[\eta]$) for the solution was computed with the help of the Huggins–Kramer relationship,¹³ and the M_v values of the polymers were calculated with the following expression:¹⁴

$$[\eta] = 2.43 \times 10^{-4} M_v^{0.75}$$

RESULTS AND DISCUSSION

Effect of the surfactant concentration

As the concentration of the anionic surfactant SDS increased (from 0.0 to 0.03M) in the reaction medium, the rate of polymerization ($R_{p(\text{obs})}$) and the percentage of the AN conversion increased (Fig. 1). In an aqueous medium, the surfactant molecules above their CMC aggregated to form micelles, leading to a biphasic system, that is, bulk a phase and a micellar phase.¹⁵ Because of hydrophobic interactions, the solubilization of AN in the micellar core was greater.¹⁶ Furthermore, the concentration of Cr(VI) increased at the Stern layer of the SDS micelle because of the electrostatic attraction between them, and the solubilization of CH in the micellar core was greater because of hydrophobic interactions.^{9,12,16} As a result, a greater number of free radicals were produced, and this led to rate enhancement (Table I). The reduction in the rate and percentage of the AN conversion in the presence of CTAB was due to the electrostatic repulsion of Cr(VI) by the Stern layer of the cationic ion. Narain et al.¹⁷ reported a similar trend for acrylamide polymer-

ization with potassium persulfate as an initiator, and this was also supported by Shukla and Mishra.⁶ The rate of Cr(VI) consumption ($-R_{\text{Cr}}$) increased with an increasing SDS concentration and decreased with the CTAB concentration, as reported in our earlier work for other redox systems.¹²

Effect of the AN concentration

$R_{p(\text{obs})}$ was square-dependent on the monomer concentration in the presence of 0.015M SDS, and this was confirmed from a bilogarithmic plot of $R_{p(\text{obs})}$ versus the AN concentration (Fig. 2). The square dependence of the rate on the AN concentration indicated that the process was linearly terminated.¹⁸ A similar type of behavior was reported earlier for a redox system with Cr(VI).¹⁹ At a high concentration of AN in the reaction

TABLE I
Effect of Surfactant Concentration on the Rates

[Surfactant] (mmol/L)	$R_p \times 10^5$ (mol L ⁻¹ s ⁻¹)		$-R_{\text{Cr}} \times 10^6$ (mol L ⁻¹ s ⁻¹)	
	SDS	CTAB	SDS	CTAB
0	6.89	—	2.21	—
5	6.98	3.12	2.39	1.08
10	10.12	1.11	5.13	0.59
15	13.23	1.01	7.82	0.57
20	16.29	1.02	10.42	0.59
25	18.95	1.03	12.79	0.55
30	20.12	1.01	13.75	0.55

[AN] = 0.518 mol/L; [Cr(VI)] = 5.08 mmol/L; [CH] = 0.108 mol/L; [H⁺] = 0.498 mol/L; μ = 0.6 mol/L; temperature = 35°C.

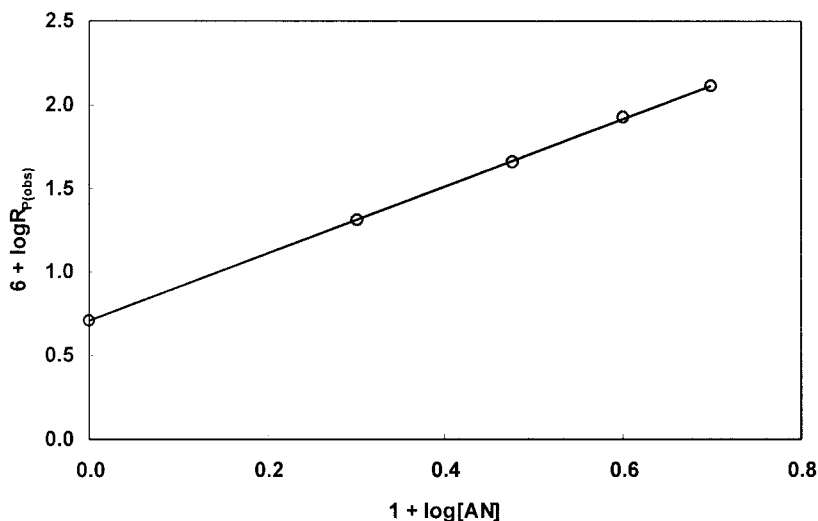


Figure 2 Plot of $\log R_{p(obs)}$ versus $\log [AN]$. $[SDS] = 0.015M$; $[Cr(VI)] = 5.01 \times 10^{-3}M$; $[CH] = 0.108M$; $[H^+] = 0.498M$; $\mu = 0.6M$; temperature = $35^\circ C$.

mixture, a greater number of AN molecules were available at the reaction site, and this led to rate enhancement. $-R_{Cr}$ was independent of the monomer concentration.

Effect of cr(VI)

With an increasing Cr(VI) concentration (from 2.5 to 12.5 mM) at a constant concentration of SDS in the reaction medium, $R_{p(obs)}$ and the percentage of the monomer conversion decreased. Cr(VI) influenced both the initiation and termination processes. Perhaps under our experimental conditions, it acted better as a terminator than as a initiator at higher concentrations.

A plot of the reciprocal of $R_{p(obs)}$ versus the Cr(VI) concentration is linear (Fig. 3), indicating linear termination.²⁰ R_{Cr} also increased with an increasing Cr(VI) concentration in the presence of 0.015M SDS. The slope obtained from a double-logarithmic plot of $-R_{Cr}$ versus the Cr(VI) concentration (not shown) was computed to be 1.12, which confirmed the first-power dependence of $-R_{Cr}$ on the Cr(VI) concentration.

Effect of the CH concentration

The rate of polymerization and the percentage of the AN conversion increased linearly with an increasing concentration of CH (0.05–0.25M) in the reaction mix-

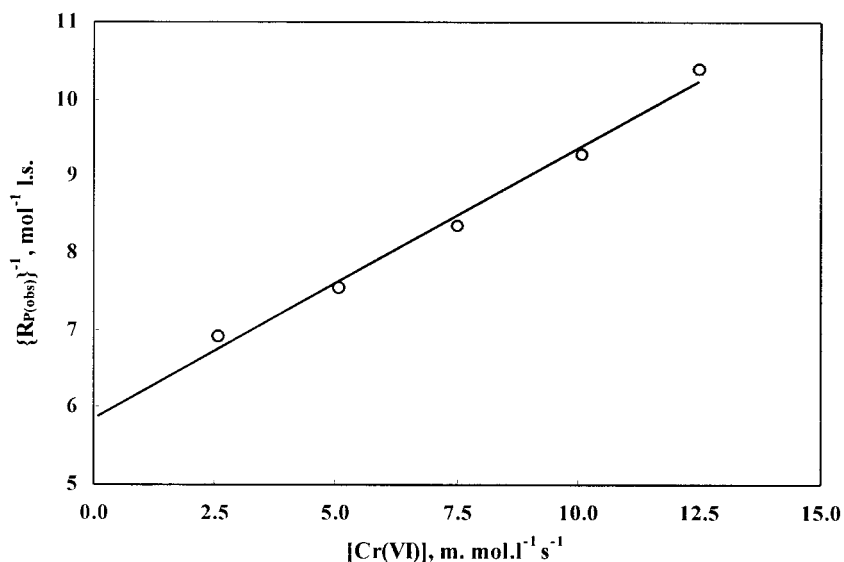


Figure 3 Dependence of the reciprocal of $R_{p(obs)}$ on the concentration of Cr(VI). $[SDS] = 0.015M$; $[AN] = 0.518M$; $[CH] = 0.108M$; $[H^+] = 0.498M$; $\mu = 0.6M$; temperature = $35^\circ C$

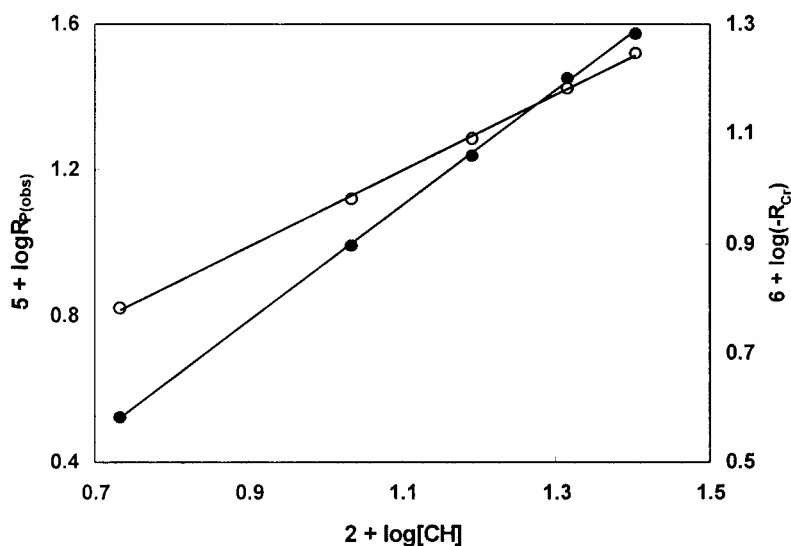


Figure 4 Plot of (○) $\log R_{p(\text{obs})}$ and (●) $\log(-R_{Cr})$ versus $\log [CH]$. [SDS] = 0.015M; [AN] = 0.518M; [Cr(VI)] = $5.01 \times 10^3 M$; $[H^+] = 0.498 M$; $\mu = 0.6 M$; temperature = 35°C.

ture at a constant SDS concentration (i.e., 0.015M). A bilogarithmic plot of $R_{p(\text{obs})}$ versus the CH concentration (Fig. 4) produces a slope of 1.08. The solubilization of CH in the micellar core was greater at a higher concentration, and this led to an increase in the number of the free-radical formation.¹⁶ Thus, an enhancement of the rate was observed for an increase in the CH concentration. Similarly, $-R_{Cr}$ was linearly dependent on the CH concentration, and this agreed with the value of the slope (i.e., 1.15) of the bilogarithmic plot of $-R_{Cr}$ versus the CH concentration (Fig. 5).

Effect of the H^+ concentration and ionic strength (μ)

$R_{p(\text{obs})}$ increased with an increasing H^+ concentration at a constant value of μ (0.6M; Table II) in a 0.015M SDS solution. The localization of the H^+ concentration at the Stern layer of micelles of SDS at its higher concentration,¹⁷ beyond its CMC, increased the oxidizing power of Cr(VI), leading to rate enhancement. $-R_{Cr}$ was also observed to increase with the H^+ concentration. An increase in μ (0.5–0.8M) of the reaction medium at a constant H^+ concentration (0.5M) en-

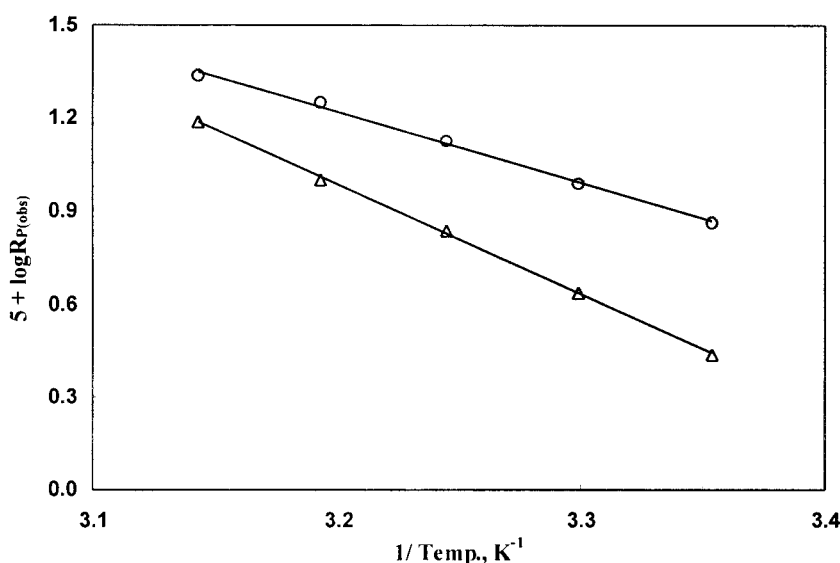


Figure 5 Arrhenius plot of $\log R_{p(\text{obs})}$ versus the reciprocal of the temperature. [SDS] = (○) 0.015M or (●) 0.000M; [AN] = 0.518M; [CH] = 0.108M; [Cr(VI)] = $5.01 \times 10^3 M$; $[H^+] = 0.498 M$; $\mu = 0.6 M$.

TABLE II
Effect of the $[H^+]$ Concentration and μ on the Rates

$[H^+]$ (mol/L)	μ (mol/L)	$R_p \times 10^5$ (mol L ⁻¹ s ⁻¹)	$-R_{Cr} \times 10^6$ (mol L ⁻¹ s ⁻¹)
0.102	0.6	12.48	6.73
0.191	0.6	12.67	7.01
0.311	0.6	12.93	7.28
0.405	0.6	13.11	7.63
0.498	0.6	13.23	7.82
0.498	0.7	13.32	7.89
0.498	0.8	13.47	8.09

[SDS] = 0.015 mol/L⁻¹; [AN] = 0.518 mol/L⁻¹; [Cr(VI)] = 5.08 mmol/L⁻¹; [CH] = 0.108 mol/L⁻¹; temperature = 35°C.

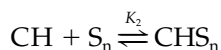
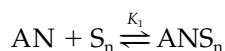
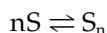
hanced $R_{p(\text{obs})}$ in the presence of 0.015M SDS, and this was in good agreement with the earlier report.²¹ The increase in μ also increased $-R_{Cr}$.

Effect of the temperature

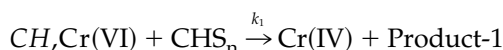
When the temperature increased from 25 to 45°C, an amelioration of the polymerization rate was observed, both in the absence and in the presence of 0.015M SDS in the reaction medium. At the higher temperature, a better solubilization of CH in the micellar phase caused the rate enhancement. From an Arrhenius plot (Fig. 5), the overall activation energy for the polymerization processes was computed to be 16.01 and 10.46 kcal/mol in the absence and presence of 0.015M SDS, respectively. A decrease of 5.55 kcal/mol in the activation energy supported the positive catalytic role of the surfactant.^{9,12,16,18}

Reaction mechanism and kinetic scheme

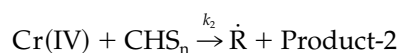
On the basis of all the aforementioned facts, a free-radical mechanistic scheme is proposed for the polymerization process as follows (where R represents the primary radical, S represents the surfactant, S_n represents the micelles, and k_i^m , k_p^m , and k_t^m are rate constants; superscript m indicates the micellar phase):



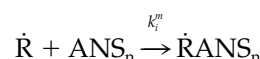
For the reaction of Cr(VI) with



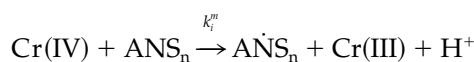
For the formation of the free radical,



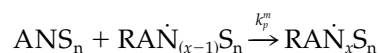
For initiation by the primary radical,



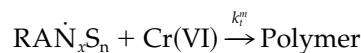
For initiation by Cr (IV),



For propagation,



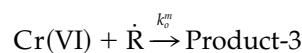
For linear termination:



For mutual termination,



For the reaction of R with Cr(VI),



With a steady-state assumption for the free radical, an expression for the rate of polymerization (R_p^m) and the rate of Cr(VI) consumption ($-R_{Cr}^m$) can be derived as follows. For linear termination,

$$R_p^m = \frac{k_p^m [ANS_n]^2}{k_t^m} \left\{ \frac{k' [CHS_n]}{[ANS_n] + \left(\frac{k_o^m}{k_i^m}\right) Cr(VI)} + k_i^{m'} \right\} \quad (1)$$

$$-R_{Cr}^m = 2[Cr(VI)]\{k' [CHS_n] + k_i^{m'} [ANS_n]\} \quad (2)$$

Where k' is equal to $k_1 k_2$. For mutual termination,

$$R_p^m = \frac{k_p^m [ANS_n]^3 [Cr(VI)]^{1/2}}{(k_i^m)^{1/2}} \times \left\{ \frac{k' [CHS_n]}{[ANS_n] + \left(\frac{k_o^m}{k_i^m}\right) Cr(VI)} + k_i^m \right\}^{1/2} \quad (3)$$

$$-R_{Cr}^m = [Cr(VI)]\{k' [CHS_n] + k_i^{m'} [ANS_n]\} \quad (4)$$

In the presence of CH, it seems likely that its reaction with Cr(IV) is preferred to that between Cr(IV) and the monomer.¹⁸ Therefore, the term $k_i^{m'}$ can be ruled out; this is also confirmed by the observation that $-R_{Cr}$ was independent of the AN concentration.²² The reciprocal of $R_{p(obs)}$ was linearly dependent on the concentration of Cr(VI), and this indicated favorable conditions for linear termination;²⁰ that is, mutual termination was ruled out. As a result, the rate expression can be written as follows:

$$R_p^m = \frac{k_p^m [ANS_n]^2}{k_t^m} \left\{ \frac{k' [CHS_n]}{[ANS_n] + \left(\frac{k_o^m}{k_i^m}\right) Cr(VI)} \right\} \quad (5)$$

$$-R_{Cr}^m = 2\{k' [Cr(VI)] [CHS_n]\} \quad (6)$$

or

$$R_p^m = \frac{k_p^m k_1 [AN]^2 [S_n]^2}{k_t^m} \left\{ \frac{k' k_2 [CH] S_n}{k_1 [ANS_n] + \left(\frac{k_o^m}{k_i^m}\right) [Cr(VI)]} \right\} \quad (7)$$

$$-R_{Cr}^m = 2\{k' k_2 [Cr(VI)] [CH] [S_n]\} \quad (8)$$

$R_{p(obs)}$ can be considered the sum of the rate of polymerization in the bulk phase (R_p^b) and that in the micellar phase (R_p^m): $R_{p(obs)} = R_p^b + R_p^m$. However, at higher concentrations of SDS above its CMC, $R_{p(obs)}$ can be assumed to be R_p^m . Thus, rearranging eq. (7) gives the following:

TABLE III
Effect of SDS Concentration on M_v

[SDS] (mmol L ⁻¹)	[η] (g ⁻¹ L)	$M_v \times 10^{-4}$
0	0.94	6.07
5	0.96	6.24
10	1.11	7.58
15	1.35	9.84
20	1.52	11.58
25	1.67	13.07
30	1.75	13.91

[AN] = 0.518 mol/L⁻¹; [Cr(VI)] = 5.08 mmol/L⁻¹; [CH] = 0.108 mol/L⁻¹; [H⁺] = 0.498 mol/L⁻¹; μ = 0.6 mol/L⁻¹; temperature = 35°C.

$$\frac{1}{R_{p(obs)}} = \frac{k_t^m}{k_p^m k' k_1 k_2 [AN] [CH] [S_n]^2} \times \left\{ \frac{k_t^m \left(\frac{k_o^m}{k_i^m}\right) [Cr(VI)]}{k_p k' k_1 k_2 [AN]^2 [CH] [S_n]^2} \right\} \quad (9)$$

Constant parameter

The constant k_1 in the presence of AN was computed from a plot of R_{Cr} versus the Cr(VI) and CH concentrations (not shown) to be 7.82×10^{-4} and 7.69×10^{-4} , respectively, upon the substitution of $K_2 = 9.87 \times 10^4$ mol⁻¹ L and S_n , which was determined from as follows: $S_n = (C_D - CMC)/N$, where the aggregation number N was taken to be 62.¹⁵ The values of k_o^m/k_i^m and k_p^m/k_t^m were found to be 3.71 and 0.45, respectively, from a plot of $1/R_{p(obs)}$ versus the Cr(VI) concentration (Fig. 3) with the following relationship from a modification of eq. (9):

$$\left(\frac{k_o^m}{k_i^m}\right) = \left(\frac{\text{Slope}}{\text{Intercept}}\right) \times k_1 [AN] [S_n] \quad (10)$$

$$\left(\frac{k_p^m}{k_t^m}\right) = \frac{1}{(\text{Intercept}) \times k' k_1 k_2 [AN] [CH] [S_n]^2} \quad (11)$$

Molecular weight

In the presence of the anionic surfactant SDS, M_v for the polymer increased as the SDS concentration increased in the reaction mixture (Table III). This may have been due to a better environment, which assisted in lengthening the polymer chain.^{9,12} Such trends have been observed by others for AN polymerization with other redox systems.¹⁶

CONCLUSIONS

The presence of SDS, an anionic surfactant, in the reaction medium enhanced the rate of polymerization

and the percentage of the monomer conversion. This was attributed to the micellar coulombic and hydrophobic interactions for Cr(VI), the monomers, and CH. The presence of CTAB, a cationic surfactant, reduced the rates considerably because of the electrostatic repulsion of Cr(VI) by a positively charged Stern layer. The polymer M_v also increased with an increasing concentration of the anionic surfactant micelles.

The authors thank UGC (New Delhi, India) and DST (New Delhi, India) for DRS-SAP and FIST sponsoring. One of the authors (M.P.) is thankful to CSIR (India) for an RA position.

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